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Thermoplastic starch modified during melt processing with organic acids: The effect of molar mass on thermal and mechanical properties

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ABSTRACT

Thermoplastic starch (TPS) was modified with ascorbic acid and citric acid by melt processing of native starch with glycerol as plasticizer in an intensive batch mixer at 160 °C. It was found that the molar mass decreases with acid content and processing time causing the reduction in melting temperature (T_m). As observed by the results of X-ray diffraction and DSC measurements, crystallinity was not changed by the reaction with organic acids. T_m depression with falling molar mass was interpreted on the basis of the effect of concentration of end-chain units, which act as diluents. FTIR did not show any appreciable change in starch chemical compositions, leading to the conclusion that the main changes observed were produced by the variation in molar mass of the material. We demonstrated that it is possible to decrease melt viscosity without the need for more plasticizer thus avoiding side-effects such as an increase in water affinity or relevant changes in the dynamic mechanical properties.

1. Introduction

Thermoplastic starch (TPS) is one of the most promising bio-based materials available for biodegradable plastic production. Its importance is growing in face of the environmental problems caused by petrochemical synthetic polymers and to the expected rise in the cost of petroleum-based materials. However, TPS suffers from several limitations, such as poor mechanical properties and water sensitivity and much research has been published on this subject (Averous, 2004; Bastioli, 1998; Carvalho et al., 2003, 2005; Da Róz et al., 2006; Dean et al., 2008; Jiugao et al., 2005; Mathew and Dufresne, 2002; Roper and Koch, 1990; Sarazin et al., 2008; Teixeira et al., 2005). Chemical modification of TPS by reactive extrusion with organic acids such as ascorbic acid (AA) (Carvalho et al., 2005) and citric acid (CA) (Carvalho et al., 2005; Ma et al., 2009; Ning et al., 2007a, 2007b, 2007c, 2009; Shi et al., 2007, 2008) have been successfully used to produce TPS with modified properties. This kind of chemical modification is very attractive, because it can be performed by a continuous solvent-free method making this a green process. TPS modification by citric acid has been successfully used to inhibit starch re-crystallization (i.e. retrogradation) (Jiugao et al., 2005), improve the plasticization process and to increase the compatibility between TPS and other polymers, such as for example poly(lactic acid) (PLA) (Ning et al., 2007a, 2007b). However, the main effect of processing TPS in the presence of organic acid is the controlled reduction of its molar mass which can be used to change its properties, such as the glass transition temperature (T_g), crystalline melting point (T_m) and melt viscosity. After processing, the organic acid can be neutralized, leading to a stable composition.

In a previous study (Carvalho et al., 2005), we reported on TPS melt processing in the presence of glycerol, ascorbic acid and citric acid, carried out to promote the chemical modification of starch, generating new materials, differing from the standard glycerol-plasticized TPS. The results showed that the use of non-volatile and non-toxic acids as catalysts provides the additional advantages of health safety and food compatibility. To the best of our knowledge, only our work has described the use of ascorbic acid for TPS modification, although this is an interesting option because of its non-toxicity and the possibility of its use in active food packaging material, due to its antioxidant properties.

In this paper we report a study of citric acid (CA) and ascorbic acid (AA) modified TPS, by high-performance size exclusion chromatography (HPSEC), dynamic-mechanical analysis (DMA), X-ray diffraction (XDR), differential scanning calorimetry (DSC), water absorption (WA) and infrared spectroscopy (FTIR). The behavior of the glass transition temperature (T_g), determined by DMA and crystalline melting point (T_m) were correlated with the molar mass of the processed starch.

2. Materials and methods

2.1. Materials

Regular native cornstarch containing 28% amylose and 11% moisture (Amidex 3001) was obtained from Corn Products Brazil.

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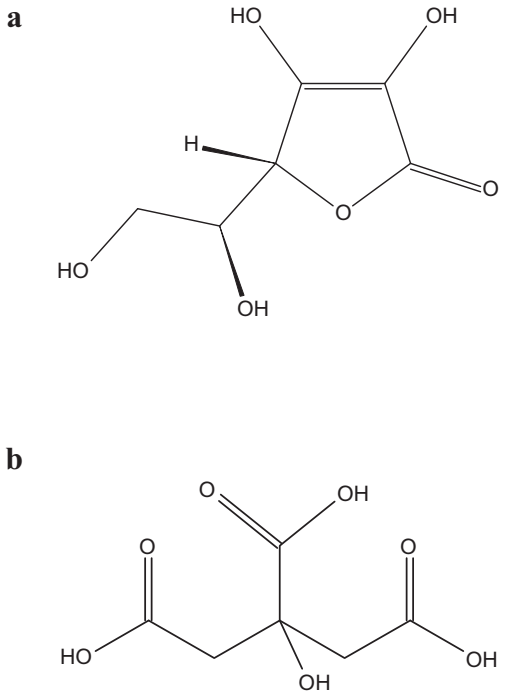

Fig. 1. Chemical structures of (a) ascorbic acid and (b) citric acid.

Reagent grade ascorbic acid, citric acid, glycerol and stearic acid were used as received. The chemical structures of the organic acids used are presented in Fig. 1.

2.2. Reactive processing of thermoplastic starch

Starch and glycerol were premixed to a homogeneous material. The mixtures were then processed at 160 °C in a Haake Rheomix 600 batch mixer equipped with roller rotors at 50 rpm. Two mixing times were used, 6 and 15 min. A small amount of stearic acid (0.5 wt%) was added as a processing agent. The processed samples were hot pressed at 150 °C into 2 mm thick plates. The proportions of the materials are given on dry weight basis.

2.3. Dynamic mechanical analysis (DMA)

DMA measurements were performed on a DMA 242C Netzsch dynamic mechanical analyzer working in the tension mode with 11 mm between sample holders. Measurements were performed under flowing air at frequency of 1 Hz, with a maximum dynamic force of 7 N, amplitudes up to 16 μm and heating rate of 3 °C/min. The samples ($45 \times 5 \times 2\,mm^3$) were cut from the hot-pressed molded plates.

2.4. High-performance size exclusion chromatography (HPSEC)

HPSEC was carried out at 35 °C as previously described (Carvalho et al., 2003) in a three Ultrahydrogel column (300 mm × 7.8 mm i.d.) system. Detection was performed using a refractive index detector. The eluent was 0.1 M sodium nitrate adjusted to pH 11.5 with NaOH solution. The calibration standards were Pullulan (polymaltotriose) with molar masses of 180, 738, 5800, 12,200, 23,700, 48,000, 100,000, 212,000, 380,000 and 1,600,000. The starch samples were dissolved in a 1 M sodium hydroxide solution by stirring for 2 h, and the resulting solutions filtered through a 1 μm glass fiber filter.

2.5. Fourier transform infrared spectroscopy (FTIR)

Attenuated total reflection (ATR) infrared spectra were recorded in a Nicolet Nexus 470 spectrophotometer equipped with a Nicolet Specular-ATR module, with zinc selenide crystal (45°), 4 cm^{-1} resolution. Each spectrum was collected form and 64 scans.

2.6. X-ray diffraction (XDR)

The TPS samples were conditioned at 25 °C and 53% relative air humidity (RH) for 30 days before the measurements. Diffractograms were recorded on a Rigaku diffractometer. Scattered radiation was detected in the Bragg-angle (2θ) range of 3–40° at a speed of 28°/min. The extent of crystallinity was estimated by the height ratio between the V-type diffraction peak at $2\theta = 19$ and the baseline of the diffractograms at $2\theta = 6.7$ (Hulleman et al., 1999).

2.7. Water absorption (WA)

Prior to the measurements, samples were dried at 110 ± 1 °C for 12 h and then placed in containers with relative humidity of 53 and 97%, at 25 °C. The relative humidity environment was produced with saturated solutions of $Mg(NO_3)_2$ and K_2SO_4, respectively, as stipulated in ASTM E-104 (1985). The amount of water absorbed was measured by weighing the samples until constant mass was reached, which took at least one week.

2.8. Differential scanning calorimetry analysis (DSC)

Differential scanning calorimetry was carried out in a Shimadzu DSC 50 calorimeter. The analyses were performed under nitrogen flowing at 20 mL/min, at a heating rate of 10 °C/min, using around 30 mg of sample in aluminum pans. Before analysis, the samples were heated at about 180 °C and quenched in liquid nitrogen, to freeze the thermoplastic starch in the amorphous state. The glass transition temperature determined graphically as the temperature corresponding to the midpoint in the change in calorific capacity during transition (T_g).

3. Results and discussion

The processing of thermoplastic starch in the presence of the organic acids, whose structures are shown in Fig. 1, was very dependent on the organic acid concentration. As the organic acid concentration increases, the mixtures display lower viscosity and greater tack stickiness. This effect can be correlated with the reduction of molar mass since the addition of higher quantities of plasticizers does not have a similar effect on viscosity and stickiness. It was observed that the addition of either CA or AA produced clearer mixtures than those produced without acids. However, the mixtures with AA showed a tendency to become yellow to brown on storage, probably due to the color of the oxidation products of ascorbic acid.

Fig. 2 shows the FTIR spectra for TPS. The main absorption bands were observed at 3400–3450 cm^{-1} (hydroxyl groups), 2880–2900 cm^{-1} (C–H stretching) and 1150–1085 cm^{-1} (ether band). Very little variation was seen among the spectra for the samples of each composition, showing that the modification of properties was due to chain scission alone. If some modification of functional groups did occur, it was at a low extension and not detected by FTIR. In fact, some low degree of esterification probably takes place, as observed by Shi et al. (2007) in TPS processed in the presence of high concentrations of CA.

The weight average molar mass (M_w) and number average molar mass (M_n) data, derived from HPSEC measurements, are presented in Table 1. The molar mass decreases with increasing acid content

Table 1
Data for TPS composition, time of processing, glass transition temperature determined by DMA (T_g), weight and number average molar weight (M_n and M_w), water absorption (WA), crystallinity (X_c) and peak melting temperature (T_m), heat of fusion (ΔH_f) and range of melt temperatures determined by DSC (T_{onset} and T_{end}).

Sample #	Acid	Acid content (wt%)	Time (min)	T_g (°C)	M_w ($\times 10^{-6}$)	M_n ($\times 10^{-5}$)	WA (%)		X_c	ΔH_f (J/g)	T_m (°C)	T_{onset}(°C)	T_{end} (°C)
							53%RH	97%RH					
00	None	–	6	92	1.64	1.41	11.6	60.0	0.80	120.8	150	140	228
01	Ascorbic	0.5	6	63	1.3	1.29	11.2	42.0	0.82	121.4	184	173	250
02	Ascorbic	1.0	6	64	1.24	1.22	11.4	61.0	0.82	113.5	189	180	240
03	Ascorbic	1.0	9	58	0.37	0.87	11.2	62.0	0.84	126.6	177	151	237
04	Ascorbic	1.0	12	49	0.34	0.76	11.5	64.0	0.80	126.2	166	165	243
05	Ascorbic	1.0	15	78	0.77	0.56	11.4	60.0	0.77	126.7	172	171	238
06	Ascorbic	1.5	6	58	0.67	0.54	11.7	66.0	0.81	109.2	175	174	249
07	Ascorbic	2.0	6	41	0.37	0.53	11.7	62.0	0.78	122.8	171	161	227
08	Ascorbic	3.0	6	56	0.25	0.46	11.8	66.0	0.76	124.5	172	172	239
09	Citric	1.0	6	58	0.19	0.41	11.6	59.0	0.82	126.0	166	165	230
10	Citric	2.0	6	58	0.08	0.25	11.6	58.0	0.77	117.2	147	124	215

and time of processing this being responsible for the reduction in the melt viscosity and for the change in macroscopic behavior, such as the degree of apparent tack (Carvalho et al., 2005).

The water absorption (WA) experiments, presented in Table 1, showed that neither the chemical modification nor the presence of the organic acids in the TPS compositions affected the water absorption, as usually occurs when more plasticizer, such as glycerol, is added (Carvalho et al., 2002). This result showed that water absorption, which is a critical parameter in TPS compositions, is not affected by the molar mass of the starch in the plasticized material. This result was not expected, since water is a plasticizer for TPS and its affinity with TPS would rise as the starch molar mass decrease, at least in the range of molar mass studied. It was demonstrated that the melt viscosity of TPS can be lowered by molar mass reduction, without the need to add plasticizer and without changing its water absorption properties. Note that the data for water absorption at 97% relative humidity shows more variation than at 53% RH. This fact can be attributed to the formation of a watery phase on the specimens, increasing the error in those measurements.

The crystallinity observed in the X-ray diffraction patterns shown in Fig. 3 and the estimated crystallinity index (X_c) presented in Table 1 are apparently not affected by processing conditions and no relation between molar mass of starch and crystallinity was evident in the range of molar mass investigated. This data shows that the changes in the properties of TPS produced by processing in the presence of acids are mainly caused by effects other than crystallization after processing.

From the DSC experiments were determined the melting transitions temperatures for TPS which data are presented in Table 1. The glass transition was not detected, because this transition is usually

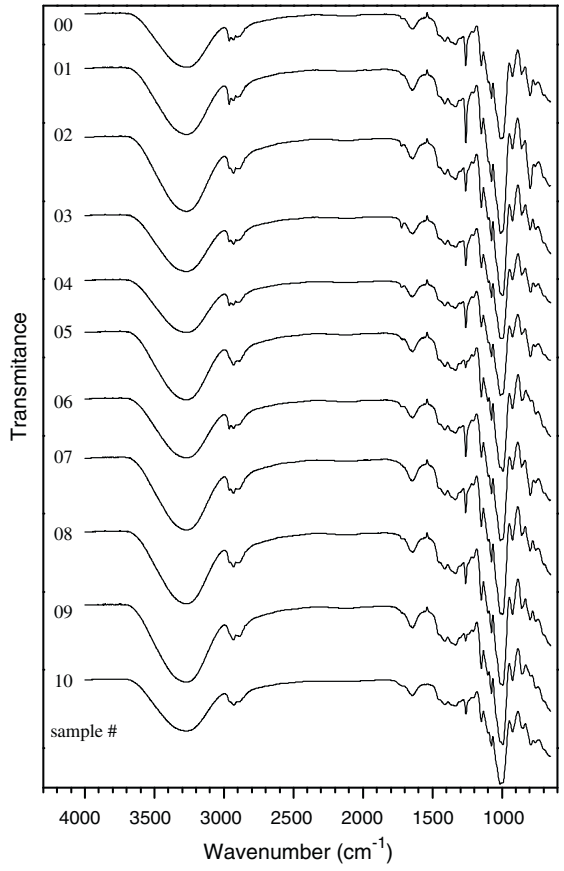

Fig. 2. FTIR spectra of the thermoplastic starch prepared by melt processing native starch in the presence of glycerol as plasticizer and ascorbic and citric acids.

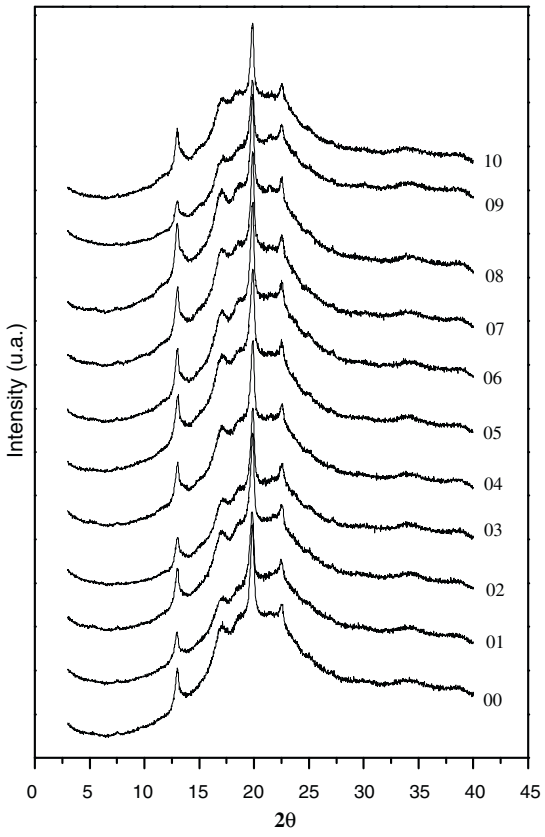

Fig. 3. X-ray diffraction patterns of thermoplastic starch prepared by melt processing native starch in the presence of glycerol as plasticizer and ascorbic and citric acids.

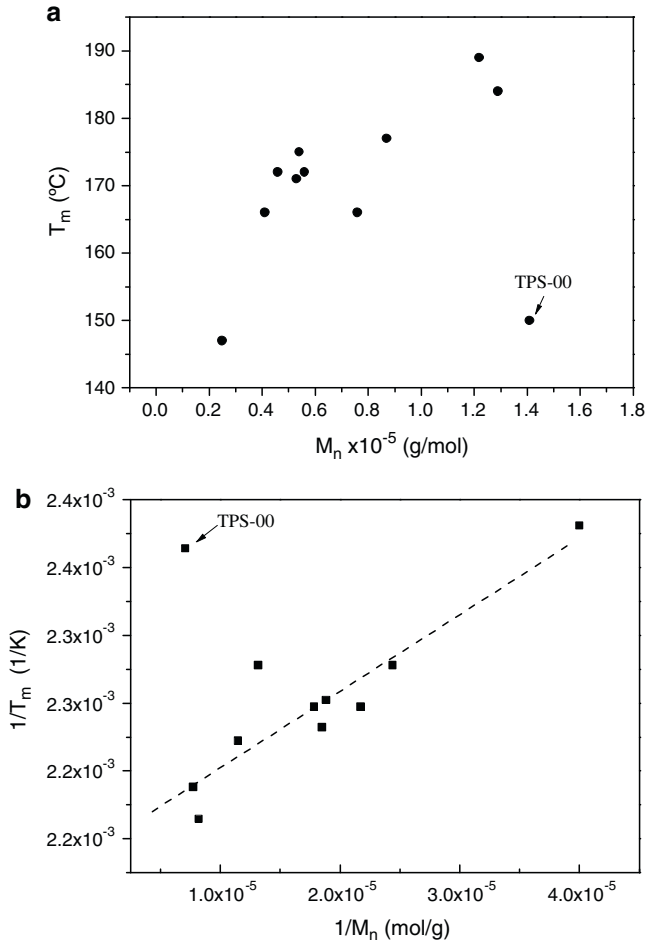

Fig. 4. (a) Melt peak temperature, T_m, plotted against number-average molar mass (M_n) and (b) $1/T_m$ plotted against $1/M_n$.

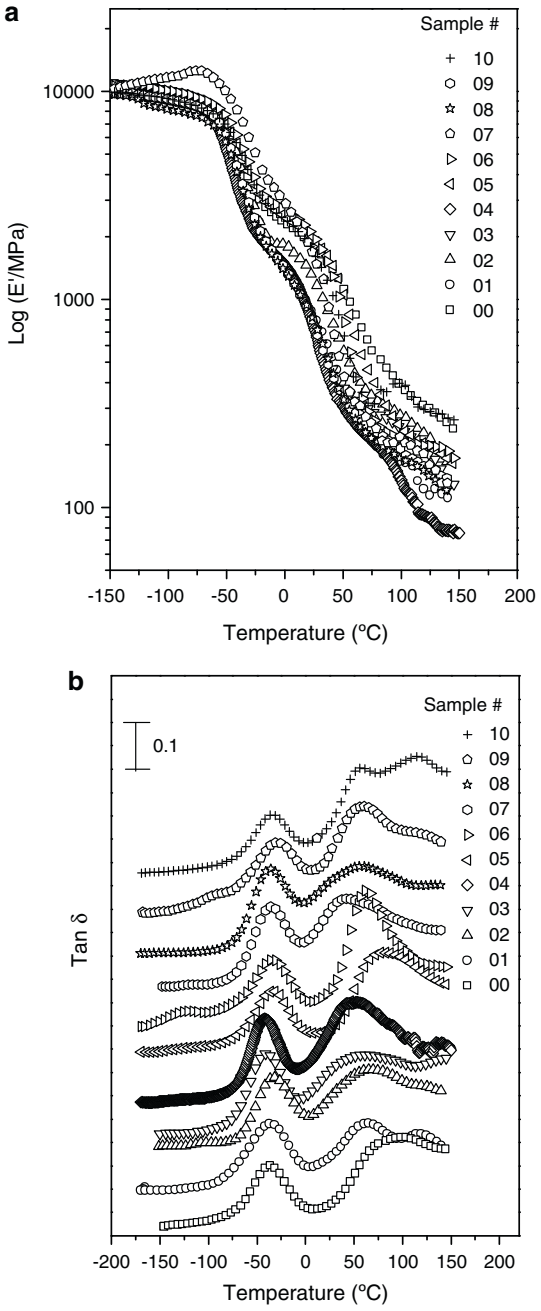

Fig. 5. Storage modulus (E') and loss tangent ($\tan\delta$) of TPS samples plotted against temperature.

difficult to be observed in TPS. Melting of the residual acid (153 °C for CA and 192 °C for AA) did not affect the results, owing to its low concentration. The heat of fusion (ΔH_f) determined from the DSC endothermic peaks for each sample is presented in Table 1. ΔH_f is almost the same for all samples, with a value of approximately 120 J/g. This result is in consistence with the X-ray diffraction results and confirms the observation that the crystallinity indices of the samples are similar and independent of the processing conditions and the organic acid concentration. The diffraction patterns for all samples are similar, and can be seen in Fig. 3, which means that no variation in crystalline structure was produced among the processed samples. Notwithstanding the heat of fusion being independent of the processing conditions and the acid concentration, the melt temperatures (T_m, T_{onset} and T_{end}) are quite dependent on the acid content and as a consequence on the molar mass of starch in TPS.

Fig. 4a shows the dependence of T_m on M_n for the TPS processed under various conditions. Except for the TPS processed in the absence of added acid (marked with an arrow), melting temperature decreases approximately monotonically as the average molar mass (The same behavior was observed for M_w.) decreases, showing a direct relation between M_n or M_w and T_m in the range of molar mass investigated.

This lowering of the melting temperature as the molar mass falls may be explained in two ways, given that the melting point of a crystalline phase in a polymer can be normally depressed by two mechanisms, (i) the decrease in the size of crystallite (lamella thickness) and (ii) the presence of an impurity (solvent for example) (Flory, 1953). No evidence of varying crystallite size was observed in the X-ray diffraction patterns. On the other hand, the monomeric unit at the end of the chain can be considered different in chemical nature from the *mers* along the chain and the melting point can depend on the molar mass, as a particular case of (ii), where the *mer* unity at terminal chain is considered an impurity. The depression of the melting point temperature due to the molar mass can be predicted by Eq. (1) (Sperling, 2006).

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_f}\frac{2M_0}{M_n} \quad (1)$$

where T_m is the actual melting temperature, T_m^0 is the melting temperature for the polymer in the pure state, which in this case means a polymer of infinite molar mass, R is the gas constant and $2M_0/M_n$ is the mole fraction of the chain ends, M_0 being the molar mass of

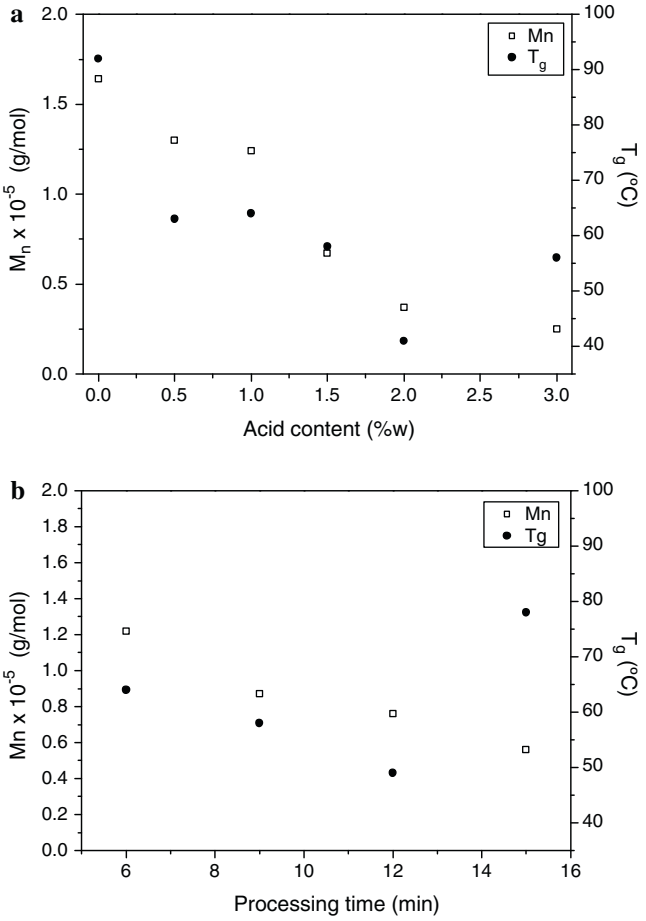

Fig. 6. Correlation of number-average molar mass (M_n) and glass transition temperature (T_g) for TPS samples with (a) ascorbic acid content for TPS samples processed for 6 min and (b) processing time for TPS processed in the presence of 1 wt% ascorbic acid (TPS 02, 03, 04, 05).

the terminal *mer*. A similar equation can be used to describe the depression of the melting point by the addition of a diluent, such as glycerol in TPS (Flory, 1949, 1953). The effect of diluents was here kept constant, as the glycerol content was maintained constant at 30% by weight in all the TPS mixtures.

Fig. 4b shows the dependence of $1/T_m$ on $1/M_n$. Taking ΔH_f as invariable, Eq. (1) foreseen a linear relation were the intercept at $1/T_m$ axis corresponds to $1/T_m^0$. The experimental data shows that Eq. (1) works reasonably well, except for TPS00 which, as already observed, shows a distinct behavior from the modified TPS. The value of T_m^0 estimated by the intercept is 465 K (192 °C).

The unmodified TPS (TPS-00) which had the highest molar mass showed a behavior that diverged from that widely observed in the acid-modified starch, whose T_m was related to M_n by a monotonic curve. One possible reason for this could be the fact that the crystalline structure of unmodified TPS is mainly due to the amylopectin fraction in which crystallization occurs between adjacent *A* chains (Robin et al., 1974). With the extensive chain breaking due to hydrolysis, this kind of crystal structure which size is limited by the amylopectin structure is no longer formed and the crystallization of TPS is dominated by the free chains cleaved during starch hydrolysis. This result leads to the conclusion that the amylopectin dendrimer structure (Matheson and Caldwell, 1999) is probably destroyed by acid hydrolysis, leading to more linear structures that crystallize in a similar way to linear synthetic polymers.

Fig. 5a and b shows the variation of the logarithm of the storage modulus (E') and tan δ with temperature, respectively. The storage modulus curve for TPS reveals two thermal relaxations, a low temperature transition between −60 and −50 °C, attributed to the glycerol-rich phase (Averous and Bouquillon, 2004; Forssel et al., 1997) and a second transition occurring above room temperature, related to the starch-rich phase and corresponding to the glass transition temperature of TPS. As TPS is a semicrystalline polymer, beyond the glass transition temperature, a plateau can be seen, where the modulus decreases slowing, due to the presence of the plasticizer. Above the melting temperature there is the onset of the viscous regime and the modulus drops, hindering its measurement. In general, the modulus *versus* temperature profiles are similar among the samples with similar behavior even beyond the glass transition. This occurs because the plateau beyond T_g of semicrystalline polymers depends on the crystallinity index which was similar for all samples. This result also shows that crystallinity is more determinant in establishing the plateau beyond T_g than molar mass, for TPS. Two reasons can be suggested for this: (i) the molar mass (even after hydrolysis) is sufficiently high to make the TPS rubbery plateau independent of M_w and M_n, and (b) the high polarity of TPS makes it a highly cohesive material, where motion in the rubbery state is limited.

Fig. 6a and b shows the relationship between the acid content and the processing time, respectively with both M_n and T_g. (The relation with M_w was similar to that observed with M_n.)

Observing the materials processed for a fixed time of 6 min (Fig. 6a), it is possible to see that as the acid content increases M_n decreases. Fig. 6b shows that M_n falls with processing time up to 12 min, but then shows an unexpected increase. This behavior could indicate that after 12 min of processing other processes take place, such as reaction between two or more chains, loss of water due to its evaporation and a reduction in the rate of hydrolysis by the drop in water concentration during processing.

4. Conclusions

In the present study, thermoplastic starch was melt processed in a batch mixer at 160 °C in the presence of low concentrations of ascorbic acid and citric acid, 30% glycerol as plasticizer and water at 20 wt% with respect to the starch. The samples were characterized by high-performance size exclusion chromatography, Fourier transform infrared spectroscopy, differential scanning calorimetry, X-ray diffraction, water absorption and dynamic mechanical analysis. A sharp change in TPS processing properties was observed when TPS was processed in the presence of the acids. The material showed a very low viscosity and high tack. It was demonstrated that melt viscosity properties of TPS can be altered by molar mass reduction, without the need to add more plasticizer and without changing its water absorption properties. Neither the X-ray pattern nor the crystallinity index was affected by processing in the presence of the acids and no relation was observed between these characteristics and molar mass. This result was corroborated by DSC measurements, since no variation of the heat of fusion ΔH_f (~120 J/g for all samples) was observed with the varying molar mass of the samples. By contrast, the melt temperature, T_m, showed a dependence on molar mass, which was explained by the presence of end-*mer* units at the ends of the starch chains, which differ from the *mers* that constitute the chains and act as if diluting the TPS. In the absence of acids TPS showed a distinct behavior. This work demonstrated that it is possible to change several properties of TPS, such as the melting temperature and processing characteristics, without changing fundamental properties that are critical for TPS, such as water absorption and glass transition temperature.

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